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Pressureless sintering of nanocrystalline AlN was achieved at remarkably low temperatures of 1600C and 1550C using coarse grained and nanocrystalline yttria additives, respectively. X-Ray diffraction studies showed that the nanocrystalline AlN materials obtained by our approach have a very low oxygen content, confirming FNAA results. The high purity and high density associated with our pressureless sintered undoped nanocrystalline AlN pellets gave rise to greater thermal conductivity values than hot-pressed conventional AlN. Yttria-doped nanocrystalline AlN pellets attained high density and high thermal conductivity (148 W/m-K) without resorting to special sintering conditions/treatments.

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"Processing of Nanocrystalline Nitrides and Oxide Composites"

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Nanocrystalline Aluminum Nitride

In our last report [1], we described the synthesis and additive-free pressureless sintering of nanocrystalline AlN. It was found that nanocrystalline AlN could be pressurelessly sintered to >95% of theoretical density by 1700°C. In this report, we describe the effect of two different Y_2O_3 powders that were added to the nanocrystalline AlN to further enhance densification. The thermal conductivity of both the doped and undoped samples is also reported, and the influence of the oxygen content on the thermal conductivity of the undoped material is discussed.

Pressureless Sintering with Y_2O_3 additions

In order to examine the effect of sintering aids, 4 wt% of a micron-sized Y_2O_3 powder was added to the nanocrystalline AlN and the H. C. Starck Grade B AlN powders. The samples were then formed into pellets, isostatically pressed at 410 MPa, and heated at 10°C/min to the sintering temperature where they were soaked for two hours. The densities of these samples were determined by Archimedes' method and are shown in Figure 1. The theoretical density for AlN samples with 4 wt% Y_2O_3 (incorporated as $Y_3Al_5O_{12}$) was calculated to be 3.33 g/cm^3, although this value would change slightly depending on which yttrium aluminate phases were present and their relative amounts. The sintering curves shown in Figure 1 are for (a) nanocrystalline AlN with 4 wt% Y_2O_3, (b) H. C. Starck Grade B AlN with 4 wt% Y_2O_3, and (c) H. C. Starck Grade B AlN without any additive. The Y_2O_3 additives have a large effect on the densification of both the nanocrystalline and commercial AlN powders. Whereas the pure commercial material did not exceed 75% of theoretical density even after sintering at 1900°C, it attained >90% of theoretical density at 1800°C with 4 wt% Y_2O_3 additives. The large increase in densification for the commercial AlN with the Y_2O_3 additions at temperatures between 1700° and 1800° was due to the well-known formation of a liquid phase in the Y_2O_3-Al_2O_3 system at temperatures around 1760°C. This liquid phase greatly increased material transport and enhanced densification. However, there was also an increase in density for the nanocrystalline samples at temperatures well below 1700°C. The addition of yttria to the nanocrystalline AlN increased the density attained at 1600°C from 78% to 93%. There were two likely mechanisms for the increased low-temperature densification of ultrafine AlN systems with Y_2O_3 additions: (a) an Al-Y-O-N liquid could form and promote material transport via liquid-phase sintering, or (b) solid-state grain boundary diffusion could increase due to Y_2O_3 doping of the grain boundaries.

It is well accepted that a ternary liquid (Al_2O_3-Y_2O_3-AlN) can be present at temperatures >1700°C [2], but our results suggest that it might form at even lower temperatures (<1600°C) or that Y_2O_3 doping of the grain boundaries significantly increases solid-state diffusion.

Although the pure AlN samples prepared in this work and by Hashimoto et al. [3] have similar sintering behaviors as described previously [1], the AlN sample prepared by Hashimoto et al. benefited more from the Y_2O_3 sintering additive. There were two possible reasons for the latter observation. The first was that Hashimoto et al. [3] used an ultrafine, high surface area Y_2O_3 powder (57 m^2/g) as the additive, whereas the Y_2O_3 used in sintering nanocrystalline AlN (Figure 1(a)) was much coarser (~1 μm diameter, 8.7 m^2/g). This could lead to significant differences in the reactivity of the Y_2O_3 with the surface oxide and nitride species of the AlN. The second explanation involves the different amounts of Y_2O_3 that were added: 4 wt% Y_2O_3 was added to the nanocrystalline AlN samples while Hashimoto et al. [3] used 2 wt% Y_2O_3. There might exist an optimal concentration of Y_2O_3 additive depending on the crystallite size and/or oxygen content of the AlN sample. Other researchers have shown that there was an optimal additive content to maximize the thermal conductivity of AlN [4,5], and the amount necessary could be affected by both the oxygen content and the powder used. This concept might extend to the densification of AlN as well.

In order to investigate these possibilities, an additional set of nanocrystalline AlN samples were sintered with 2 and 4 wt% nanocrystalline Y_2O_3 that had been synthesized by the method of Fokema and Ying [6] and had a surface area of 56.5 m^2/g. The resulting pressureless sintering curves are shown in Figure 2. The nanocrystalline Y_2O_3 additive with a high surface area enhanced the low-temperature densification of nanocrystalline AlN considerably (by ~6% of theoretical density at 1500°C), and the resulting sintering behaviors were similar to that of Hashimoto et al.'s sample for sintering temperatures ≤1550°C [3]. The different amounts of Y_2O_3 added did not appear to lead to different densification behavior. The densification to 95% of theoretical density by 1550°C with nanocrystalline Y_2O_3 was impressive; this study illustrates the effect of particle size for the Y_2O_3 additive on the sintering of nanocrystalline AlN.

One striking observation in comparing our sintering results to those of Hashimoto et al. [3] was the similarity in the densification behaviors of ultrafine, high-purity AlN powders that were synthesized and processed via very different methods. This similarity suggests that (a) these two very different processes have produced high-quality powders of very similar characteristics, or (b) a lower temperature limit for densification of AlN has been approached. To investigate the latter possibility, we note that Sternitzke and Müller [7] and Solmon et al. [8] measured the oxygen-nitrogen interdiffusion coefficient for Y_2O_3-doped polycrystalline AlN at 1600°C to be ~3x10^{-15} cm^2/s and ~3x10^{-14} cm^2/s, respectively. Although the interdiffusion coefficients are not the most desired values to compare with densification studies, nitrogen is expected to be the slowest diffusing species so that oxygen-nitrogen interdiffusion values will give an order-of-magnitude estimate for the rate-limiting step in AlN sintering. Since the activation energies reported for diffusion in AlN is very large (240-430 kJ/mol), the diffusion coefficients will decrease rapidly with temperature, making sintering even more difficult. For example, assuming an activation energy of 300 kJ/mol, the interdiffusion coefficient will decrease by an order of magnitude between 1600°C and 1400°C. At 1600°C, the oxygen-nitrogen interdiffusion coefficients are already ~4 orders of magnitude lower than the oxygen

diffusion coefficient in Al_2O_3 [7]. Compared to Y_2O_3-doped AlN, pure AlN presumably has even lower diffusion rates given its lower sinterability. Therefore, to compensate for the decrease in diffusion rate with temperature, the particle size of the nanocrystalline AlN would have to decrease by another order of magnitude to further reduce the sintering temperature below 1550°C and 1700°C for Y_2O_3-doped and pure AlN systems, respectively.

X-ray diffraction patterns of the AlN pellets sintered at 1900°C with 4 wt% coarse-grained Y_2O_3 are shown in Figure 3. Both the nanocrystalline and commercial AlN samples sintered with Y_2O_3 contained secondary phases corresponding to yttrium aluminates, but the phases present were quite different. The commercial AlN sample had both $AlYO_3$ and $Al_5Y_3O_{12}$ as secondary phases, while the nanocrystalline AlN sample contained only $Al_2Y_4O_9$ as the secondary phase. The Al:Y ratios in the secondary phases of the commercial AlN sample were between 1 and 1.7, while that of the nanocrystalline AlN sample was only 0.5. This suggested that there was considerably less oxygen available in the nanocrystalline AlN sample for the Y_2O_3 to react with, so that a low Al_2O_3-containing phase was formed. Therefore, less Y_2O_3 additive might be needed to scavenge oxygen to acceptable levels for the carefully processed, higher purity nanocrystalline AlN than for the commercial AlN. The secondary phases detected by XRD of nanocrystalline AlN pellets sintered with 2 wt% and 4 wt% nanocrystalline Y_2O_3 were the $Al_5Y_3O_{12}$ and $Al_2Y_4O_9$ phases, respectively. As a comparison, Hashimoto et $al.$ [3] also found that $Al_5Y_3O_{12}$ was present as the secondary phase when only 2 wt% Y_2O_3 was added to their most sinterable, lowest oxygen-containing (2 wt%) AlN powders.

Thermal Conductivity Results

The thermal conductivity of selected samples were determined by the laser flash thermal diffusivity method by Holometrix Corporation (Bedford, Massachusetts). The samples were machined into 1/2 inch-diameter disks of 1-2 mm thick, and polished until the faces were parallel. Coating of the samples with an optical absorbing layer was necessary to prevent transmission of the laser light, especially through the highly translucent specimens. The thermal conductivity K of a sample can be obtained from the thermal diffusivity α as follows,

$$K = \rho C_p \alpha \qquad \text{(Equation 1)}$$

where ρ is the density of the sample as determined by Archimedes' method and C_p is the specific heat. The samples examined had been pressurelessly sintered at 1900°C for 2 hours and were >98% dense to allow for direct comparison. The density, specific heat, thermal diffusivity and the calculated thermal conductivity for two different samples are shown in Table 1.

Table 1. Laser flash thermal diffusivity results for samples pressurelessly sintered at 1900°C for 2 hours. Y_2O_3 additives used were low surface area powders.

Sample	Density (g/cm^3)	Specific Heat (J/g·K)	Diffusivity (cm^2/s)	Conductivity (W/m·K)
Nano AlN, no additive	3.22	0.748	0.297	71.6
Nano AlN, 4 wt% Y_2O_3	3.30	0.730	0.615	148

These thermal diffusivity results corresponded very well with results of other researchers. The two parameters that most strongly affect the thermal conductivity of undoped AlN specimens are density and oxygen content. Enloe et $al.$ [9] investigated the densification and

thermal conductivity of five different microcrystalline AlN powders processed with and without additives. As shown in Figure 4, the powders processed without additives achieved only ~70% of theoretical density through pressureless sintering, and with the exception of a single sample, had a maximum thermal conductivity of only 45 W/m·K [9]. Only by hot pressing their powders at 1900°C under 20 MPa for 1 hour were densities and thermal conductivities comparable to those reported here (the pressurelessly sintered, undoped nanocrystalline AlN is shown as • in Figure 4) obtained by Enloe et al. [9]. Hashimoto et al. [3], who has prepared an undoped AlN powder that sintered very similarly to our pure nanocrystalline powders, reported a thermal conductivity (68 W/m·K) slightly lower than that obtained here. The undoped sample prepared from H. C. Starck Grade B AlN powder was not sent out for thermal conductivity testing because it had too low a density (~73%) to merit further analysis. The oxygen content of the undoped, sintered sample prepared from nanocrystalline AlN was determined to be 0.6 wt% by FNAA. This oxygen content was considerably lower than that measured for nanocrystalline AlN powder that had been exposed briefly prior to analysis (3 wt% oxygen). Since the sintered sample of undoped nanocrystalline AlN did not have any oxide sintering aids nor detectable secondary phases, it was assumed that the oxygen impurities resided within the AlN lattice. Buhr et al. [2] plotted the thermal conductivity vs. the oxygen content for various AlN samples, along with the correlation for single-phase AlN ceramics as reported by Slack [10]. Their plot showed that the highest thermal conductivity that could be expected for AlN containing 0.6 wt% oxygen was ~100 W/m·K.

The thermal conductivities of the 4 wt% Y_2O_3-doped nanocrystalline AlN (148 W/m·K) and 4 wt% Y_2O_3-doped H. C. Starck AlN (155 W/m·K) were very similar. This was expected since the formation of a liquid phase during sintering would overwhelm any differences in the starting powders. These results for the Y_2O_3-doped samples were not only self-consistent, but were also very similar to those obtained by other researchers under similar sintering conditions. Enloe et al. [9] found that AlN doped with Y_2O_3 and sintered to >98% dense possessed thermal conductivities ranging from 125 to 160 W/m·K, depending primarily upon the oxygen content of the powder used.

Higher thermal conductivities can be attained for both undoped and doped samples by annealing them at high temperatures and for long times in a highly reducing atmosphere. Hirano et al. [11], for example, reported a thermal conductivity of 114 W/m·K for an undoped AlN sample that had been sintered at 1900°C for 8 hours in a graphite furnace. Other researchers have found that the thermal conductivity of Y_2O_3-doped AlN could be increased to ~260 W/m·K through similar heat treatments [12,13]. By heating the sample in a highly reducing atmosphere, oxygen is removed from the AlN lattice and secondary phases are gradually vaporized, thereby increasing the purity, grain size, and thermal conductivity of the AlN material.
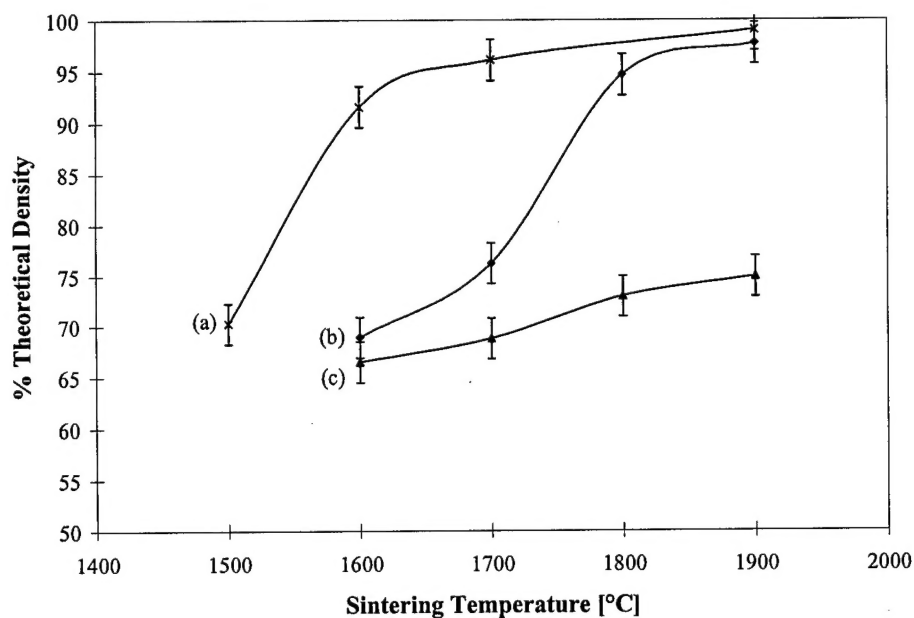
Figure 1. Pressureless sintering curves of (a) nanocrystalline AlN with 4 wt% coarse-grained Y_2O_3, and H. C. Starck Grade B AlN with (b) 4 wt% coarse-grained Y_2O_3 or (c) no additive. The samples were soaked at the sintering temperature for 2 hours.
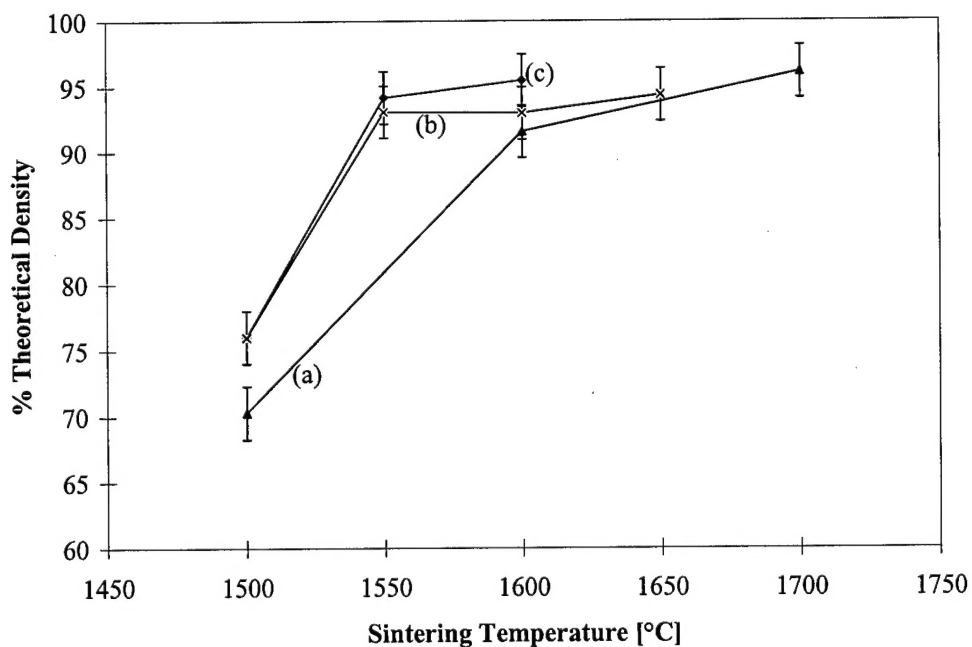

Figure 2. Sintering curves for nanocrystalline AlN with (a) 4 wt% micron-sized Y_2O_3, (b) 2 wt% nanocrystalline Y_2O_3, and (c) 4 wt% nanocrystalline Y_2O_3. The samples were soaked at the sintering temperature for 2 hours.
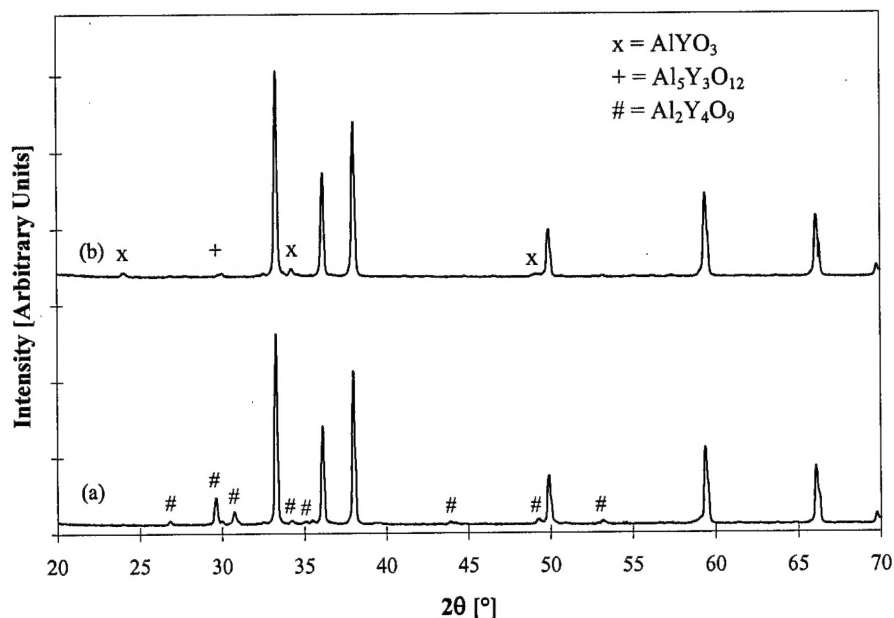
Figure 3. X-ray diffraction patterns of AlN pellets sintered at 1900°C for 2 hours with 4 wt% coarse-grained Y_2O_3. The AlN powders used were (a) nanocrystalline and (b) commercial (H. C. Starck Grade B AlN).
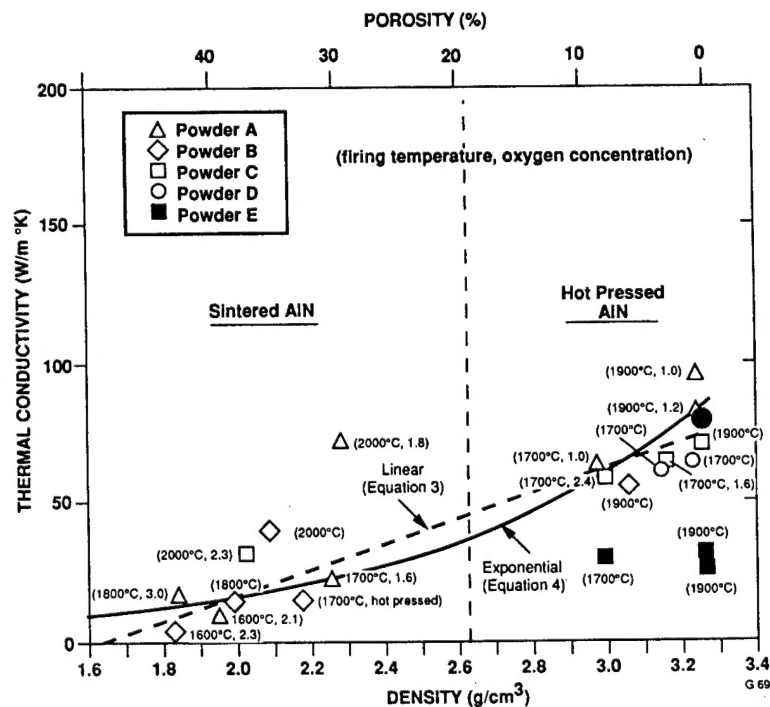

Figure 4. Thermal conductivity of additive-free pressurelessly sintered nanocrystalline AlN from this research (•) compared to that of pressurelessly sintered and hot-pressed AlN (adapted from Enloe et al. [9]).

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